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STABILIZING THE SPECTRAL PROPERTIES AND TECHNOLOGIES OF GLASS

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Sheet glass from different manufacturers or the same manufacturer but produced in different periods differ by color hue and total light transmission, which depends not only on the total content of iron oxide in the raw material and glass but also on the displacement of the equilibrium Fe(II) ⇄ Fe(III). To ensure that the molten glass, technological process, and shaping are all of high quality the equilibrium state of different forms of iron must be stabilized. Concrete recommendations on stabilizing the equilibrium and monitoring the technological process are presented.

Key words: redox potential, equilibrium of the forms of iron, chemical requirement for oxygen, technology stabilization.

Sheet glass made by different manufacturers and possessing the same light transmission (transparency) GOST 25551–77 [1] can differ by color hue — from weakly-yellow-green to blue of different intensities. The same can be observed for glass manufactured by the same manufacturer but in different periods. Such glasses will differ by the spectral light transmission, especially in the IR and UV ranges. The light transmission in the infrared region of the spectrum characterizes the heat-protection properties of the initial sheet of glass, which must be taken into account in coated-glass technology [2].

A periodic change of the color hue of molten glass is a serious reason for complication of the technological process as a result of a change in the diathermancy of the molten glass, degradation of the homogeneity of the glass, and the appearance of gaseous inclusions in molten glass which has already been fined, and problems can arise during the formation of glass articles [3 – 6].

The critical element responsible for light transmission is iron, whose permissible total content by weight according to GOST 25551–77 for sheet glass is 0.05 – 0.15%. The transparency depends on the total content of iron in the glass, while the spectral transparency depends on the displacement of the equilibrium Fe(II) ⇄ Fe(III) in either direction. Iron in the form Fe(III) lowers the light transmission in the UV region while Fe(II) does so in the IR region.

An investigation of commercial sheet glasses from different manufacturers (Table 1) showed that values of the integral light transmission are close (84.9 – 90.0% at λ = 570 nm). In the infrared region, which is responsible for the heat-engineering characteristics of glass, light transmission is sharply different (from 44.2 to 81.1% at λ = 1100 nm) (Table 2).

It is important to determine the diathermancy index (DI), given by $\mathrm{DI} = 10^{-1}\,\tau_{1100}$, where τ is the light transmission of 10 mm thick glass at wavelength 1100 nm.

The data in Table 1 were obtained by measuring the light transmission with an SF-26 spectrometer followed by reca-

TABLE 1. Characteristics of the Commercial Glasses Studied

Glass samples	Content, wt.%							Acidity unit M_a
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	Fe_2O_3	SO_3	
1, 2	74.5	0.3	8.70	0.15	15.5	0.05	0.8	3.07
3, 4	72.1	2.2	6.25	4.00	15.0	0.15	0.3	2.94
5*	73.0	0.9	9.00	3.30	13.4	0.10	0.3	2.88

* Averaged composition of float glass.

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TABLE 2. Light Transmission τ of Samples of Commercial Sheet Glasses Converted to Thickness 10 mm

Sample No. in Table 1	Light transmission τ, %				Diathermancy index
	visible range (λ = 570 nm)		IR range (λ = 1100 nm)		
	Eq. (1)	nomogram	Eq. (1)	nomogram	
1	88.1	87.9	78.2	78.0	7.8
2	90.0	90.0	81.1	80.0	8.0
3	84.2	84.9	46.2	46.8	4.6
4	84.9	85.0	44.2	45.0	4.5
5	86.6	86.4	62.4	62.0	6.2

libration of the values to 10 mm thickness using the logarithmic form of the Bouguer – Lambert – Beer equation

$$\tau = e^{-kcd}(1 - \rho^2), \tag{1}$$

where τ is the light-transmission of the glass, k is the natural absorption index, c is the concentration of the coloring additive, ρ is the intensity of the light reflection by a smooth glass surface ($D = 0.04$), and d is the thickness of the sample (mm) and from the Amosov nomogram [7].

The experimental glass samples differed by color from weak yellow-green, almost colorless (samples 1, 2) to blue with different intensity (samples 3 – 5). The samples 1 and 2 were obtained by continuous rolling, 3 and 4 by the method of vertical drawing of sheet glass, and 5 by the float-method.

The chemical compositions and spectral characteristics of the experimental glasses (Tables 1 and 2) show that the content of the iron oxides and also the redox conditions for obtaining the glasses are different. This can be judged by the color of the glass since Fe^{3+}(III) gives yellow-green glass, while Fe^{2+}(III) gives a more intense blue color but not pure blue because of the presence of Fe^{3+}(III) impurities.

In addition, evidence for more oxidative conditions of glassmaking is the introduction of $NaNO_3$ and As_2O_3 into the mix as oxidizers (samples 1 and 2) and an elevated mass content of SO_3 (0.8%) in the glass composition.

Even though the chemical compositions of the glasses are relatively close, the acid unit (M_a) calculated from the relation

$$M_a = \frac{SiO_2 + Al_2O_3}{CaO + MgO + Na_2O} \tag{2}$$

and taking account of the content of individual oxides in the glass is different and ranges from 3.07 to 2.88.

The equilibrium Fe(II) $\rightleftarrows$ Fe(III) can be displaced leftwards as the acid properties of the glass increase. However, the color and spectral characteristics (Table 2) of the glass do not agree with this proposition. Other technological factors (specifically, the redox characteristics of the raw materials, the mix, and the glassmaking conditions) play a more important role.

Thus, predominately iron in the form Fe(II) and the redox processes in the technology are responsible for the IR light transmission and heat-protection properties of the glass. The iron content in the glass must be kept constant, and it is set on the basis of the statistical data individually for each glassmaking furnace and the production line as a whole. A displacement of the equilibrium Fe(II) $\rightleftarrows$ Fe(III) affects not only the optical properties of glass but also the glassmaking and formation process and the homogeneity of the glass. The factors affecting the displacement of the equilibrium Fe(II) $\rightleftarrows$ Fe(III) are examined in detail in [8].

Basically, it should be noted that as the ratio Fe(II)/(Fe(II) + Fe(III)) fluctuates the bottom layers of the molten glass are heated or cooled and drawn into the production flow. The homogeneity of the molten glass temporarily worsens, which affects the product quality and the distribution of the molten glass in the blank workpiece during the formation of articles. The brittleness increases, the mechanical strength decreases, and the number of rejected articles increases [5, 9]. In addition, when the bottom layers of a glassmaking furnace, as a rule, more reducing, mix with the general volume of the molten glass bubbles can appear as a result of the disruption of the equilibrium of the gas phase in the different layers.

To stabilize the Fe(II) iron concentration in the glass and the technology constant monitoring must be organized in the production process in order to regulate the redox potential of the molten glass. This includes the following operations.

1. Determination of the chemical requirement for oxygen (CRO) of the raw materials. CRO characterizes the amount of reducing agents, predominately impurities, in the raw material [10, 11].

2. Determination of the CRO of the mix, including in the cullet [12].

3. Determination of the iron content in the raw material and the overall balance of the iron in the mix. To stabilize the technological process the overall balance of the iron in the mix must be constant [13]. The effect of a decrease of the overall iron balance in the glass positive — the light transmission of the glass increases, but at the same time the glassmaking process becomes more complicated and the homogeneity of the molten glass is degraded because the diathermancy of the glass increases and the bottom reducing layers, to which the access of oxygen is limited, are heated. In practice there are positive results when in such cases an iron-containing component (crocus) is added to the mix to stabilize the iron content in the molten glass [13, 14]. But this must not be done sharply but follow the tendency for the iron balance in the raw material and glass to decrease or increase.

4. Determination of the total iron content in the glass by the standard chemical method.

5. Ensuring total light (integrated) transmission of the glass in the visible region of the spectrum 400 – 740 nm.

6. Ensuring light transmission of glass in the IR region (> 740 nm) and determining the diathermancy index (DI). This index characterizes Fe(II) content indirectly on the spectrum according to the depth of the minimum at λ = 1100 nm. The Fe(II) content can be determined by a chemical method by obtaining the ratio Fe(II)/(Fe(II) + Fe(III)) [13] or by the Mössbauer method [15, 16].

7. Calculating the acidity index M_a of glass on the basis of data obtained from chemical analysis. Secondary raw materials, for example, fluorine, introduced at about 2 wt.% as a glassmaking accelerator and lowering at the glassmaking temperature the viscosity of molten glass, as well as oxidizers and reducing agents also affect the acid-base properties of the melt [11, 17]. Given the results of an analysis for FeO and Fe_2O_3 with recalibration of M_a according to Eq. (2) the Fe_2O_3 content should be taken into account in the numerator and FeO in the denominator in connection with their different role in the structure of the glass.

8. Maintaining a constant mix/cullet ratio. As the cullet in the mix increases or decreases, the amount of the oxidizers and reducing agents in the molten glass, the acid-base properties, and the redox potential of the molten glass all change.

9. Ensuring a constant coefficient of air excess α in the glassmaking furnace, since its change displaces the equilibrium Fe(II) $\rightleftarrows$ Fe(III). But the displacement of the iron equilibrium is difficult to regulate by changing α and it is dangerous from the standpoint of the entire glassmaking process.

10. Keeping the temperature – time conditions of glassmaking constant. A displacement of the equilibrium in the Fe^{2+}(II) direction ensures a temperature increase.

11. Monitoring the redox potential (ORP) of the molten glass, which especially changes when a different amount of cullet or a secondary or supporting product is introduced into the mix [18]. The Kuhnreich-Meixner O_2 sensor permits continual monitoring of the ORP of the molten glass.

Such monitoring is suggested in the technology of sheet and colorless glass or semi-white container glass and other types of articles.

The admissible deviations of the parameters listed above are established statistically and individually for each production line in combination with an analysis of the course of the glassmaking process, molding, and quality of the glass produced. The stabilized optical characteristics of the initial glass likewise make it possible to regulate the coating regimes, which change the spectral characteristics of glass as a composite in a prescribed direction.

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